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(11) EP 0 442 549 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
23.10.1996 Bulletin 1996/43

(51) Int Cl.⁶: C11D 3/39

(21) Application number: 91200119.5

(22) Date of filing: 22.01.1991

(54) Aqueous liquid bleach composition

Wässrige Bleichmittelzusammensetzung

Composition de blanchiment aqueuse

(84) Designated Contracting States:
CH DE ES FR GB IT LI NL SE

(30) Priority: 13.02.1990 GB 9003200

(43) Date of publication of application:
21.08.1991 Bulletin 1991/34

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DE-A- 3 906 768

Remarks:

The file contains technical information submitted
after the application was filed and not included in this
specification

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DescriptionBackground of the invention5 1. Field of the invention

The invention relates to an aqueous liquid bleaching composition comprising a selected organic peroxy acid, which composition may be used for the bleaching of fabrics and hard surfaces.

10 2. The prior art

Quite a number of organic peroxy acids have been reported in the literature. These peroxy materials have begun to assume great commercial importance as bleaches, especially for fabrics. Many of the more effective organic peroxy acids are solid, substantially water-insoluble materials. Much of the published art has been directed at devising means for stably suspending these peroxyacids in water.

One of the early patents in the area is US 3,996,152 disclosing the suspension of substantially water-insoluble peroxyacids by non-starch thickening agents such as Carbopol 940® in an aqueous media at low pH. Suggested as suitable peroxyacid were diperazelaic, diperbrassylic, dipersebacic and diperisophthalic acids. US Patent 4,017,412 reports similar systems except that starch based thickening agents were employed. From later investigations it became evident that the thickener type systems mentioned in the foregoing patents formed gel-like matrices which exhibited instability upon storage at elevated temperatures.

When formulated at high levels, these thickeners-systems became more stable but then caused difficulties with pourability.

US Patent 4,642,198 lists an even more expansive variety of water-insoluble organic peroxy acids intended for suspension in an aqueous, low pH liquid. Herein was first disclosed the use of surfactants, both anionic and nonionic, as suspending agents for the peroxyacid particles.

The preferred peroxy material was identified as 1,12-diperoxydodecanedioic acid (DPDA) and this was employed in almost all the examples.

EP-A-0 176 124 also focusses upon surfactant suspended 1,12-diperoxydodecanedioic acid in a low pH aqueous liquid. This art informs that surfactants other than alkylbenzene sulfonate have a detrimental effect upon chemical stability of the suspensions.

EP-A-0 240 481 seemingly also finds some special significance in the use of alkylbenzene sulfonate, focusses upon DPDA, and further suggests use of magnesium sulfate as a suspension aid and peracid stabiliser.

Other surfactant suspending systems for peroxyacids are disclosed in US Patents 4,824,592 and US 4,828,747. The peroxyacids disclosed herein are of the classes disclosed in the foregoing patents with preference for DPDA.

In US Patent 4,822,510 there is suggested to use 4,4'-sulphonyl-bisperoxybenzoic acid as the solid, water-insoluble peroxyacid.

EP-A-0435379 (which forms part of the state of the art under Article 54(3) EPC) discloses bleaching detergent compositions based on aqueous suspensions of imidoperoxydicarboxylic acids, which are indicated as having enhanced stability compared with similar suspensions of DPDA. Preferred compositions that are disclosed further include certain inorganic salts and surfactants.

The aforementioned art has placed great emphasis upon optimizing the suspending systems of the liquid bleach to improve stability.

Evidently, there has been little consideration given to improving both stability and performance altogether.

Consequently it is an object of the present invention to provide an improved aqueous liquid bleach composition based upon a solid, substantially water-insoluble organic peroxy acid having improved stability and performance.

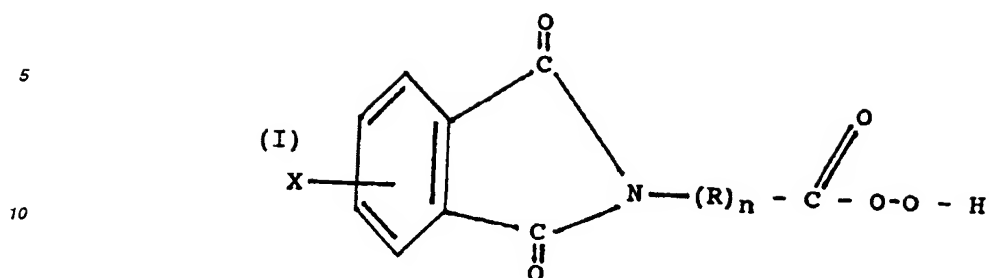
More specifically, it is an object of the present invention to provide an aqueous suspension of a solid, substantially water-insoluble organic peroxy acid, which is chemically and physically stable throughout a wide range of temperatures and which is moreover highly effective for use in the disinfecting and bleaching of substrates, e.g. fabrics and hard surfaces.

These and other objects of the present invention will become apparent as further details are provided in the subsequent discussion and Examples.

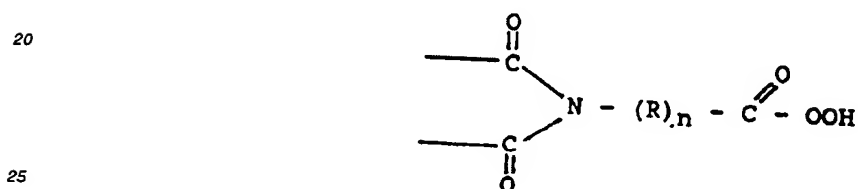
SUMMARY OF THE INVENTION

An aqueous liquid bleaching composition having a pH of from 1 to 6.5 is herein provided comprising:

(i) from 1 to 40% by weight of a solid, substantially water-insoluble peroxyacid having the general formula:



15 wherein X is H, alkyl chain, a halogen, a carboxyl group in any position on the aromatic ring, or the same peroxy-carboxylic acid group.



30 in symmetrical position to the first peroxyacid group on the aromatic ring;
R is a straight or branched chain lower alkylene having 1-4 carbon atoms, preferably -CH₂-; and
n is between 1-12, preferably 3-8;

(ii) from 2 to 50% by weight of a surfactant;

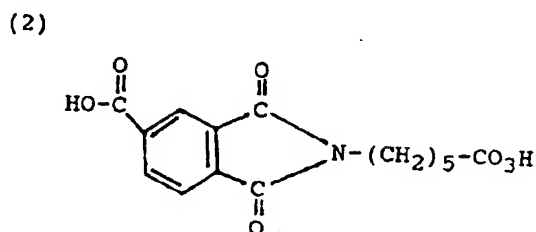
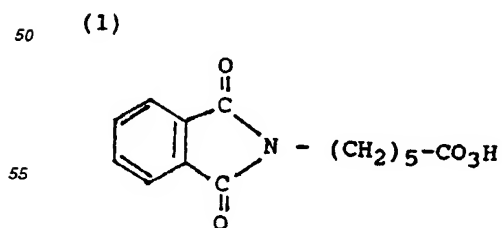
(iii) from 1.5 to 30% by weight of an electrolyte; and

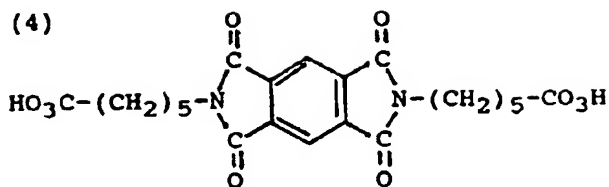
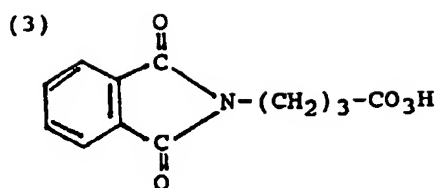
35 (iv) from 2 to 10 % by weight of hydrogen peroxide.

DETAILED DESCRIPTION OF THE INVENTION

40 It has now been found that imidoperoxycarboxylic acids of formula (I) above when presented as an aqueous suspension comprising a surfactant, electrolyte and hydrogen peroxide as hereinbefore defined at a pH within the range of 1-6.5, preferably from 2-5, are not only extremely stable both physically and chemically, but also show very effective bleaching and disinfecting properties already at low temperatures e.g. from ambient to about 40°C, as compared to similar formulations based on DPDA as the peroxyacid.

45 Preferred examples of imidoperoxycarboxylic acids usable in the present invention are those having the following structures:





of which phthaloylamino peroxy caproic acid ("PAP") of formula (1) is particularly preferred.

Amounts of this class of peroxyacids to be used in the compositions of this invention range from 1 to 40% by weight, preferably from about 2 to 30%, optimally between about 5 and 20% by weight.

The particle size of the peroxy acid used in this invention is of some importance. Particles that are too large have been found to readily separate while very small particle sizes decrease chemical stability. Advantageously the range of particle size should be from about 10 to 1,000 microns, preferably between 20 and 500 microns, optimally between 30 and 250 microns.

Surfactants are required to stably suspend the imidoperoxy carboxylic acid of the present invention. Suitable for this purpose are anionic, nonionic, cationic, zwitterionic surfactants and mixtures thereof. However, the preferred system is a mixed anionic and nonionic detergent combination.

Nonionic surfactants useful for the present invention may be selected from a wide category of materials, many of which are outlined in Schwartz, Perry Vol. II, 1958 "Detergents and Surface Agents" and Schick, vol. I, 1967 "Nonionic Surfactants". For instance, fatty acids, fatty alcohols, fatty amides and alkoxyated derivations thereof may be usefully employed. Within the alkoxyate category, there is recommended ethylene oxide and/or propylene oxide condensation products of C₈-C₂₀ linear-or branched-chain aliphatic carboxylic acids, aliphatic alcohols and alkyl phenols. Especially preferred, however, are the C₁₂-C₁₈ aliphatic alcohols ethoxylated with an average from about 3 to about 12 moles of ethylene oxide per alcohol molecule. Even more specifically the C₁₂-C₁₅ alcohols condensed with either an average of 3 or 9 moles ethylene oxide and the C₁₂-C₁₄ aliphatic alcohols condensed with 7 moles ethylene oxide have been found to be highly effective.

Anionic surfactants which may be useful for the present invention can be found listed in Schwartz, Perry, Vol. II, 1958 "Detergents and Surface Active Agents".

Examples of anionic materials are water-soluble salts of alkylbenzene sulfonates, alkyl sulfates, alkyl ether sulfates, diakyl sulfosuccinates, paraffin sulfonates, α-olefin sulfonates, α-sulfocarboxylates and their esters, alkyl glycerol ether sulfates, alkyl phenol polyethoxy ether sulfates, 2-acyloxy-alkane-1-sulfonates, β-alkoxyalkane sulfonates, secondary alkane sulfonates, and mixtures thereof.

The cationic detergents which can be used in the present invention include quaternary ammonium salts which contain at least one alkyl group having from 12 to 20 carbon atoms.

Although the halide ions are the common anions, other suitable anions include acetate, phosphate, sulfate, nitrate.

Specific cationic detergents include distearyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, stearyl trimethyl ammonium chloride coco dimethyl benzyl ammonium chloride, dicoco dimethyl ammonium chloride, cetyl pyridinium chloride, cetyl trimethyl ammonium bromide, stearyl amine salts that are soluble in water such as stearyl amine acetate and stearyl amine hydrochloride, stearyl dimethyl amine hydrochloride, distearyl amine hydrochloride, alkyl phenoxyethoxyethyl dimethyl ammonium chloride, decyl pyridinium bromide, pyridinium chloride derivative of the acetyl amino ethyl esters of lauric acid, lauryl trimethyl ammonium chloride, decyl amine acetate, lauryl dimethyl ethyl ammonium chloride, the lactic acid and citric acid and other acid salts of stearyl-1-amidoimidazoline with for instance methyl chloride, benzyl chloride and chloroacetic acid, mixtures of the foregoing.

Zwitterionic detergents include alkyl-β-iminodipropionate, alkyl-β-aminopropionate, fatty imidazolines, betaines, and mixtures thereof. Specific examples of such detergents are 1-coco-5-hydroxyethyl-5-carboxymethyl imidazoline, dodecyl-β-alanine, the inner salt of 2-trimethylamino lauric acid, and N-dodecyl-N,N-dimethyl amino acetic acid.

The total surfactant amount in the liquid bleaching composition of the invention is from 2 to 50% by weight, preferably from 5 to 35% by weight, depending on the purpose of use.

In the case of suspending liquids comprising an anionic and a nonionic surfactant, the ratio thereof may vary from about 10:1 to 1:10. The term anionic surfactant used in this context includes the alkali metal soaps of synthetic or natural long-chain fatty acids having normally from 12 to 20 carbon atoms in the chain.

Preferred surfactant mixtures usable in the present invention are mixtures of:

- i) sodium C₁₀-C₁₈ alkyl benzene sulphonate and an ethoxylated nonionic surfactant;
- ii) Sodium C₁₂-C₁₈ secondary alkane sulphonate and an ethoxylated nonionic surfactant,

Mixtures including a fatty acid, especially C₁₂-C₁₈ fatty acids, are particularly preferred.

The total level of electrolyte(s) present in the composition to provide structuring is from 1.5 to 30%, preferably from 2.5 to 25% by weight. Examples of electrolytes include inorganic compounds such as sodium sulfate and sodium nitrate, and mixtures thereof.

Since most commercial surfactants contain metal ion impurities (e.g. iron and copper) that can catalyze peroxy acid decomposition in the liquid bleaching composition of the invention, those surfactants are preferred which contain a minimal amount of these metal ion impurities. The peroxy acid instability results in fact from its limited, though finite, solubility in the suspending liquid base and it is this part of the dissolved peroxy acid which reacts with the dissolved metal ions. It has been found that certain metal ion complexing agents can remove metal ion contaminants from the composition of the invention and so retard the peroxy acid decomposition and markedly increase the lifetime of the composition.

Examples of useful metal ion complexing agents include dipicolinic acid, with or without a synergistic amount of a water-soluble phosphate salt; dipicolinic acid N-oxide; picolinic acid; ethylene diamine tetraacetic acid (EDTA) and its salts; various organic phosphonic acids or phosphonates such as hydroxyethylidenediphosphonic acid (Dequest 2010®), ethylene diamine tetra-(methylene phosphonic acid), -Dequest 2040- and diethylene triamine penta-(methylene phosphonic acid)-Dequest® 2060.

Other metal complexing agents known in the art may also be useful, the effectiveness of which may depend strongly on the pH of the final formulation. Generally, and for most purposes, levels of metal ion complexing agents in the range of from about 10-1000 ppm are already effective to remove the metal ion contaminants.

In addition to the components discussed above, the liquid bleaching compositions of the invention may also contain certain optional ingredients in minor amounts. Typical examples of optional ingredients are suds-controlling agents, such the various silicone oils, fluorescers, perfumes, coloring agents, abrasives, hydrotropes and antioxidants. However, any such optional ingredient should only be incorporated if its presence in the composition does not significantly reduce the chemical and physical stability of the peroxy acid in the suspending system.

Compositions according to the present invention include hydrogen peroxide (H₂O₂) as an essential ingredient. It has been found that hydrogen peroxide, when incorporated in the aqueous liquid bleach composition of the invention, is quite compatible with the imido peroxy carboxylic acid. Addition of hydrogen peroxide to the present bleach composition serves to provide an additional benefit of boosting its high temperature (i.e. above 60°C) bleaching performance.

In practice an amount of from 2% to 10% by weight, preferably from 4% to 6% by weight, of hydrogen peroxide in the composition achieves the desired effect.

Aqueous liquid products encompassed by the invention will have a viscosity in the range of from about 50 to 20,000 centipoises (0.05 to 20 Pascal seconds) measured at a shear rate of 21 second⁻¹ at 25°C. In most cases, however, the products of the invention will have a viscosity of from about 0.2 to about 12 PaS, preferably between about 0.5 and 1.5 PaS.

Also of importance is that the aqueous liquid bleaching compositions of this invention have an acid pH in the range of from 1 to 6.5, preferably from 2 to 5, particularly between 3.0 and 4.5.

The following Example more fully illustrates the invention. All parts, percentages and proportions referred to herein are by weight of the total composition unless otherwise stated.

40 Example

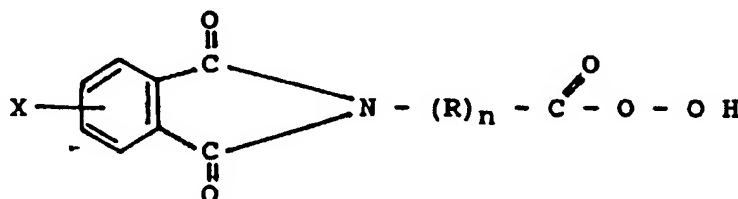
The following table shows an aqueous liquid bleach formulation within the invention which is stable and effective.

Table

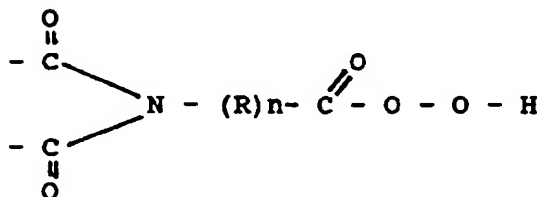
Ingredients	% by weight
Secondary C ₁₃ -C ₁₇ alkane sulphonate	6.5
C ₁₂ -C ₁₅ primary alcohol/3 ethylene oxide	1.5
C ₁₂ -C ₁₆ fatty acid	1.0
Anhydrous sodium sulphate	3.8
PAP	5.0
Dequest® 2010 (polyphosphonate)	0.07
H ₂ O ₂	5.0
Water + sulphuric acid to adjust pH to 3.5 - 4.5	Balance

Claims

1. An aqueous liquid bleaching composition having a pH of from 1 to 6.5, and comprising from 1 to 40% by weight of a solid, particulate, substantially water-insoluble organic peroxyacid, from 2 to 50% by weight of a surfactant and from 1.5 to 30% by weight of an electrolyte, wherein said organic peroxyacid is an imidoperoxydicarboxylic acid having the formula:



wherein X is H, alkyl chain, a halogen, a carboxyl group in any position in the aromatic ring, or the same peroxy-carboxylic acid group

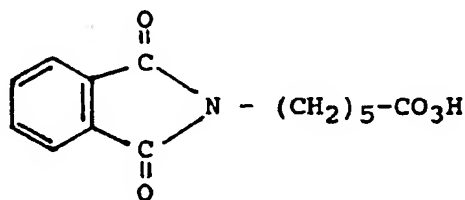


in symmetrical position to the first peroxyacid group on the aromatic ring;

R is a straight or branched chain lower alkylene having 1-4 carbon atoms, preferably -CH₂-; and n is an integer from 1-12, preferably from 3-8;

characterized in that the composition further comprises hydrogen peroxide in an amount of from 2 to 10 % by weight.

2. A composition according to claim 1, wherein said peroxyacid is phthaloylaminoperoxydicaproic acid having the formula:



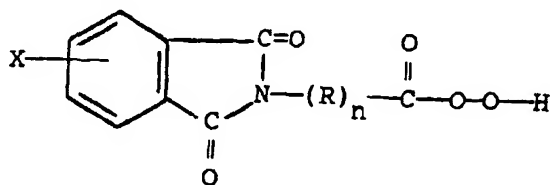
3. A composition according to claim 1 or claim 2, wherein said surfactant comprises a surfactant mixture selected from mixtures of:

- sodium C₁₀-C₁₈ alkyl benzene sulphonate and an ethoxylated nonionic surfactant; and
- sodium C₁₂-C₁₈ secondary alkane sulphonate and an ethoxylated nonionic surfactant.

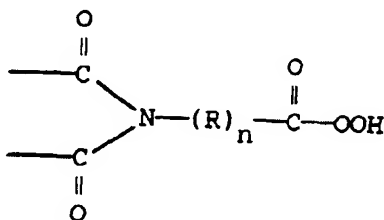
4. A composition according to claim 3, wherein said surfactant mixture further includes a fatty acid.

Patentanspruch

1. Eine wässrige flüssige Bleichmittelzusammensetzung mit einem pH-Wert von 1 bis 6,5, und enthaltend von 1 bis 40 Gewichtsprozent einer festen, teilchenförmigen, im wesentlichen wasserunlöslichen organischen Peroxysäure, von 2 bis 50 Gewichtsprozent eines Surfactants und von 1,5 bis 30 Gewichtsprozent eines Elektrolyts, worin die organische Peroxysäure eine Imidoperoxycarbonsäure der nachfolgenden Formel



ist, worin X H, eine Alkylkette, ein Halogen, eine Carboxylgruppe in irgendeiner Stellung an dem aromatischen Ring, oder dieselbe Peroxycarbonsäuregruppe

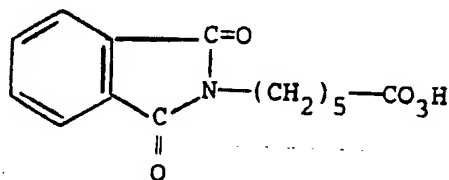


in symmetrischer Stellung zu der ersten Peroxysäuregruppe an dem aromatischen Ring ist,

R ein geradkettiges oder verzweigt-kettiges niedriges Alkyl mit 1 bis 4 Kohlenstoffatomen, bevorzugterweise $-CH_2-$ bedeutet, und n eine ganze Zahl mit einem Wert von 1 bis 12, bevorzugterweise von 3 bis 8, ist,

dadurch gekennzeichnet, daß die Zusammensetzung ferner Wasserstoffperoxid in einer Menge von 2 bis 10 Gewichtsprozent enthält.

2. Eine Zusammensetzung nach Anspruch 1, worin die erwähnte Peroxysäure Phthaloylaminoperoxycaprinsäure der nachfolgenden Formel ist:



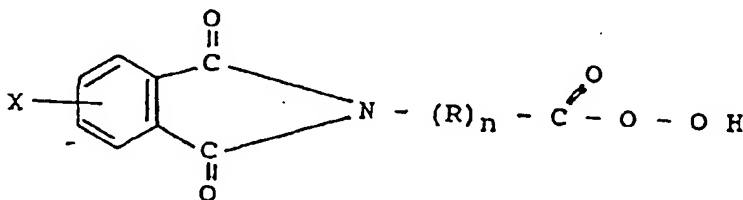
3. Eine Zusammensetzung nach einem der Ansprüche 1 oder 2, worin das Surfactant eine Surfactant-Mischung umfaßt, ausgewählt aus Mischungen von:

- (i) Natrium-C₁₀₋₁₈-alkylbenzolsulfonat und ein ethoxyliertes nichtionisches Surfactant, und
- (ii) Natrium-C₁₂₋₁₈-sek.-alkansulfonat und ein ethoxyliertes nichtionisches Surfactant.

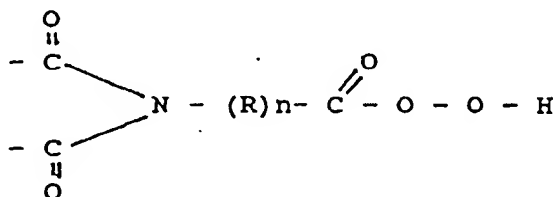
4. Eine Zusammensetzung nach Anspruch 3, worin die Surfactant-Mischung ferner eine Fettsäure enthält.

Revendications

1. Composition de blanchiment liquide aqueuse ayant un pH de 1 à 6,5 et comprenant de 1 à 40% en poids d'un peroxyacide organique solide, particulière, sensiblement insoluble dans l'eau, de 2 à 50% en poids d'un tensioactif et de 1,5 à 30% en poids d'un électrolyte, dans laquelle ledit peroxyacide organique est un acide imidoperoxy-carboxylique répondant à la formule :



dans laquelle X est H, une chaîne alkyle, un halogène, un groupe carboxyle en toute position sur le noyau aromatique ou le même groupe peroxy-carboxylique

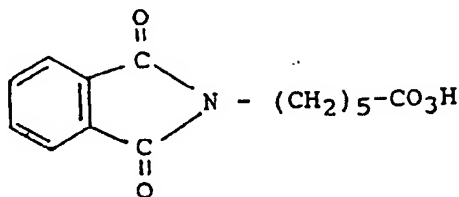


en position symétrique au premier groupe peroxyacide sur le noyau aromatique ;

R est un alkylène inférieur à chaîne droite ou ramifiée ayant de 1 à 4 atomes de carbone, de préférence -CH₂- et n est un nombre entier de 1 à 12, de préférence 3 à 8,

caractérisée en ce la composition comprend en outre du peroxyde d'hydrogène en une quantité de 2 à 10% en poids.

2. Composition selon la revendication 1, dans laquelle ledit peroxyacide est l'acide phthaloylaminoperoxy-caproïque répondant à la formule :



3. Composition selon la revendication 1, dans laquelle ledit tensioactif comprend un mélange tensioactif choisi parmi les mélanges de :

- (i) alkyl(C₁₀₋₁₈)benzènesulfonate de sodium et un tensioactif non ionique éthoxylé ; et
- (ii) alcanesulfonate secondaire de sodium en C₁₂₋₁₈ et un tensioactif non ionique éthoxylé.

4. Composition selon la revendication 3, dans laquelle ledit mélange tensioactif comporte en plus un acide gras.

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